

## DEVELOPMENT OF AN ACID-BASE-NEUTRAL SEPARATION SCHEME AND ITS APPLICATION TO ALTERNATIVE FUEL MIXTURES

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### INTRODUCTION

Alternative fuels, such as solvent-refined coal (SRC), shale oil, and biomass, are gaining more importance as energy sources, as the scarcity of crude oil increases. Fractionation of these fuels into acidic, basic and neutral components is a generally accepted method of separation that has been widely applied for the characterization of coal-derived liquids (1-6) and shale oil (7,8). Various schematics have been utilized for this kind of separation, among which aqueous extraction (1,7,10,11), ion exchange chromatography (6,9,12) and selective isolation of N-containing compounds by HCl-precipitation (2,3,5) or organometallic-coordination chromatography (6,12,13) have been the most commonly used.

Many of these schematics possess a number of disadvantages and/or limitations. The limited solubility of the protonated bases in the aqueous acid (aqueous acid extraction) (11,14) and the selective precipitation of the aromatic bases by HCl (HCl precipitation) (15) are just examples. The work by several authors (10,11,14,15) demonstrates that the basic fractions generated by different base isolation methods are not identical, and in some cases possess significant structural differences (15).

The inadequacy of the existing methods, in their present form, suggested to us that there is a need for a general and integrated acid base-neutral separation schematic. Such a schematic should be applicable to various kinds of liquid fuels, should avoid any extraction or precipitation steps and rely instead on chromatography. We have undertaken the development of this separation scheme using a large number of standards that represent the various chemical classes generally found in liquid fuels.

One "silica gel modified with KOH" column and one cation exchange resin column were employed for the fractionation. Mixtures of the various standards, as well as the alternative fuels, were separated into acids, bases and neutrals fractions which were then characterized by Gas Chromatography/Mass Spectrometry (GC/MS).

### EXPERIMENTAL

#### Preparation of the packing materials for column-chromatography

Amberlyst 15, the cation-exchanger utilized, and the silica treated with KOH, were prepared according to the literature (9,16). In this work, 20 gm of the

cation-exchange resin, slurried in tetrahydrofuran; and 20 gm of the KOH treated silica, slurried in isopropanol-chloroform mixture, each was mechanically stirred for 30 minutes before being introduced into a 500 x 11 mm I.D. glass column fitted with a teflon stopcock and a piece of glass wool to retain the packing material. The modified silica column was then washed with 100 ml of chloroform while the resin column with 100 ml of n-hexane, each solvent of which serving as a first eluent.

#### Fractionation of standard mixtures on both columns

Separate mixtures of acids, bases and neutrals standards were prepared so as to contain 300 mg/ml of tetrahydrofuran. The composition of these standards appears in Table 1. The retention behaviour of the separate mixtures, on both columns, was monitored gravimetrically (and later studied by GC/MS) by injecting 1 ml of each mixture on each of the two columns and collecting fractions in vials of 5 ml each. Fractions were evaporated to constant weight by placing the vials in a, home-made, water bath-heated block, set at 70°C and passing Nitrogen at a low pressure. Figure 1 outlines the schematic used to fractionate a total mixture of the standards, and later applied to the liquid fuels, along with the eluents utilized to provide the optimum conditions for the separation.

#### Gas Chromatography-Mass Spectrometry: Experimental Conditions

The GC/MS system used was an HP 5995 B equipped with a library search system. The mass spectrometer was used in the electron impact (EI) mode with an ionization potential of 70 eV. Gas Chromatographic conditions appear as a footnote in Table 1. Standards were chromatographed individually and in their respective mixtures of acids, bases or neutrals to determine their retention characteristics and the best resolution conditions.

#### RESULTS & DISCUSSION

Chromatogram 1 shows the total mixture of acids, bases and neutrals standards before fractionation, while chromatograms 2, 3 and 4 are for the acidic, basic and neutral fractions, respectively, after the total mixture has been successively separated on cation-exchange and silica modified columns, according to the developed schematic in Fig. 1. Chromatograms 2 - 4 were generated under identical chromatographic conditions for comparison purposes. These conditions along with peak numbers identification appear in Table 1.

Chromatogram 1, in addition to being complex, shows that co-elution of several of the components is inevitable, even with the slow temperature program employed. These problems are overcome after the total mixture is fractionated, as chromatograms 2 - 4 confirm.

Chromatogram 2 shows that the acidic fraction is pure; no overlap of basic or neutral components has been detected by GC/MS. Chromatogram 3 demonstrates that the basic fraction is slightly contaminated with some acidic components (peaks 31, 33, 39 and 41). The contamination levels are low as indicated by the relative peak areas measurement. The only contamination of the neutral components, in this same chromatogram, comes from 2-methyl indole (peak 34). This compound behaves as a weak base and can easily be trapped by a strong cation-exchanger. This phenomenon is further emphasized in chromatogram 4 for the neutral fraction which shows the complete absence of 2-methyl indole.

The strong overlap of 2-sec-butylphenol (peak 24) and 3-t-butylphenol (peak 25) with the neutral fraction in chromatogram 4, could be due to the steric hindrance of the bulky buthyl groups to adsorption of these respective phenols on the basic silica surface.

Chromatogram 5 shows a basic fraction isolated from a typical Brazilian SRC (Mina do Leão) using the developed schematic. Conditions are the same as in Table 1 except that a 50C/min temperature program was used.

A portion of the total ion chromatogram (T.I.C.) for this same fraction is displayed in chromatogram 6. Both the gas chromatogram and the total ion chromatogram indicate that the various basic components have been well resolved which makes their identification (not attempted) quite possible specially knowing that this fraction should contain the basic compounds as the results in chromatogram 3 indicate.

In conclusion, this work suggests that using the developed schematic any mixture containing acidic, basic and neutral components can be effectively separated into its respective chemical classes, with a minimum overlap among these classes. The method can be refined a little more so as to yield even purer fractions. Work along these lines is under study.

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TABLE 1- Composition of Standards Utilized for Preparative Acid-Base-Neutral Separation. Numbers Correspond to Peaks in Chromatograms 1-4\*

| PEAK<br>NUMBER | COMPONENT                       | PEAK<br>NUMBER | COMPONENT                    | PEAK<br>NUMBER | COMPONENT                    |
|----------------|---------------------------------|----------------|------------------------------|----------------|------------------------------|
| 1              | Cyclohexyl Acetate              | 15             | 8-Methyl-Quinoline           | 29             | 3-t-Butyl Phenol             |
| 2              | Phenetole                       | 16             | Phenol                       | 30             | 2-Amino Teralin              |
| 3              | 5-Ethyl, 2-Methyl Pyridine      | 17             | O-Cresol                     | 31             | P-Methoxy Phenol             |
| 4              | Benzyl-Ethyl-Ether              | 18             | Diphenyl Ether               | 32             | Indole                       |
| 5              | N, N-Dimethyl Aniline           | 19             | 1,2,3,4-Tetrahydro-Quinoline | 33             | m-Methoxy Phenol             |
| 6              | 2,3-Dihydro,2-methyl-Benzofuran | 20             | 2,6-Dimethyl-Quinoline       | 34             | 2-Methyl Indole              |
| 7              | 2,3-Dihydro-Benzofuran          | 21             | P-Cresol                     | 35             | 2,3-Dimethyl Indole          |
| 8              | N-Methyl Aniline                | 22             | 1-Indanol                    | 36             | Dibenzothiophene             |
| 9              | Aniline                         | 23             | 4-Ethyl Phenol               | 37             | 7,8-Benzoquinoline           |
| 10             | 2,4-Dimethyl Aniline            | 24             | 2-Sec-Butyl Phenol           | 38             | Acridine                     |
| 11             | O-Ethyl Aniline                 | 25             | 2-Phenyl-Pyridine            | 39             | 2-Naphthol                   |
| 12             | Benzyl Alcohol                  | 26             | 3-Phenyl-Pyridine            | 40             | 1,2,3,4-Tetrahydro-Carbazole |
| 13             | 2-Amino Pyridine                | 27             | Dibenzofuran                 | 41             | Resorcinol                   |
| 14             | Quinoline                       | 28             | Capric Acid                  | 42             | Carbazole                    |

\* CHROMATOGRAPHIC CONDITIONS: 50 m x 0.2 mm I.D. Fused Silica Carbowax 20 M Capillary; Column Temperature: 60°C Isothermal for 5 min, then 2°C/min temperature program to 240°. Flame Ionization Detector 280°C; Injector 250°C. Carrier Gas Helium at 1 ml/min. Split Ratio 1:15.

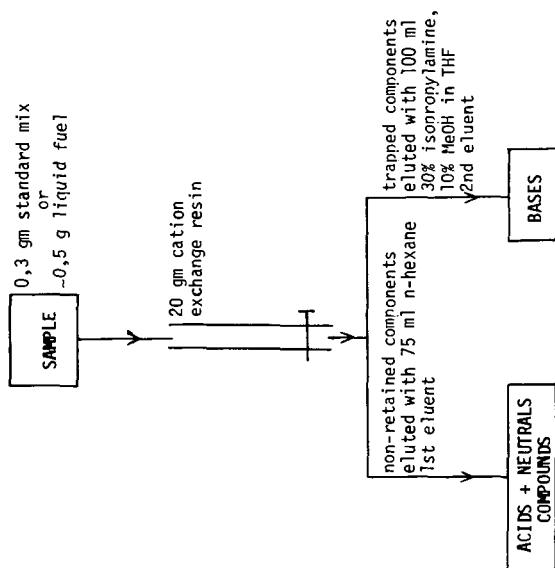
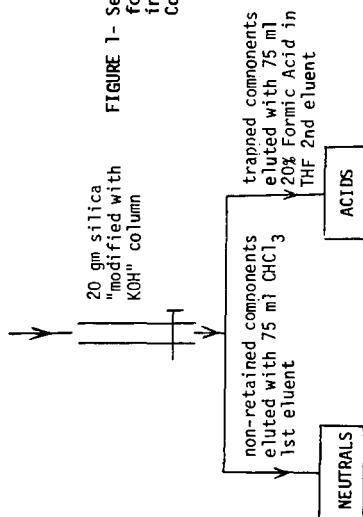


FIGURE 1- Separation Scheme Developed  
for Fractionating Liquid Fuels  
into Acids, Bases and Neutrals  
Components.



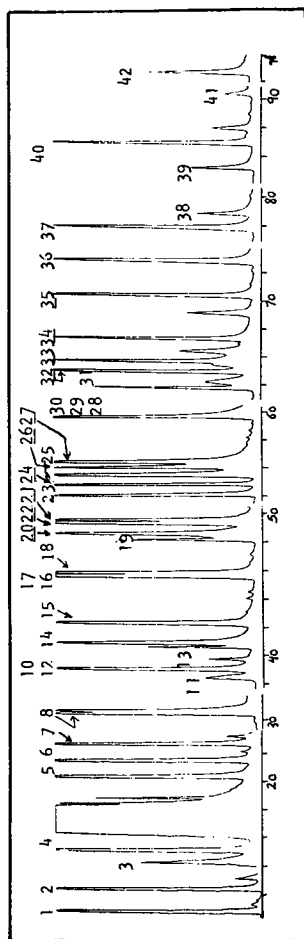


Figure 1. TOTAL MIXTURE OF ACIDS, BASES AND NEUTRALS STANDARDS BEFORE FRACTIONATION.  
CONDITIONS SAME AS TABLE 1.

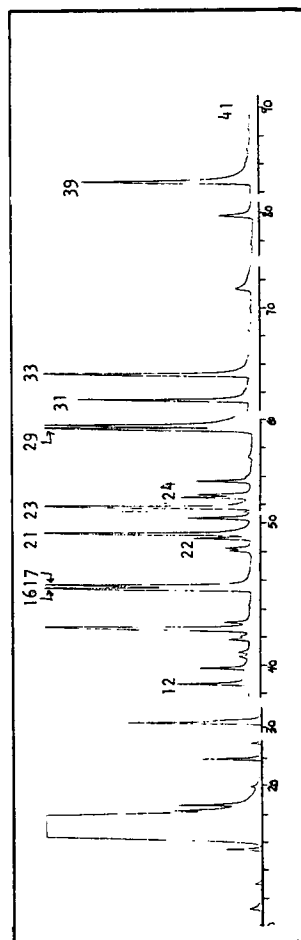


Figure 2. ACID FRACTION OBTAINED AFTER FRACTIONATION. CONDITIONS SAME AS TABLE 1.

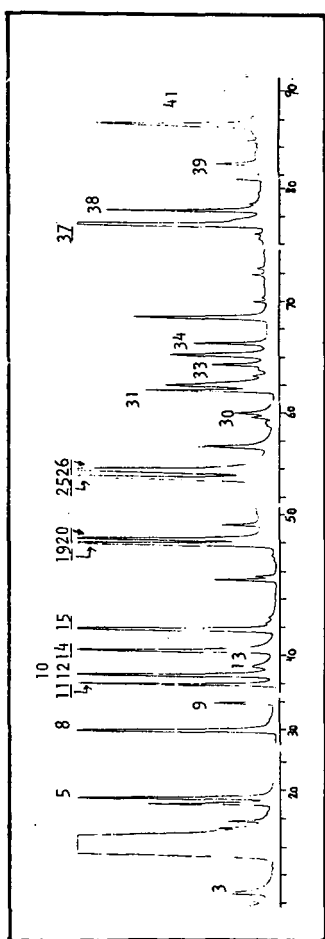


Figure 3. BASIC FRACTION OBTAINED AFTER FRACTIONATION. CONDITIONS SAME AS IN TABLE 1.

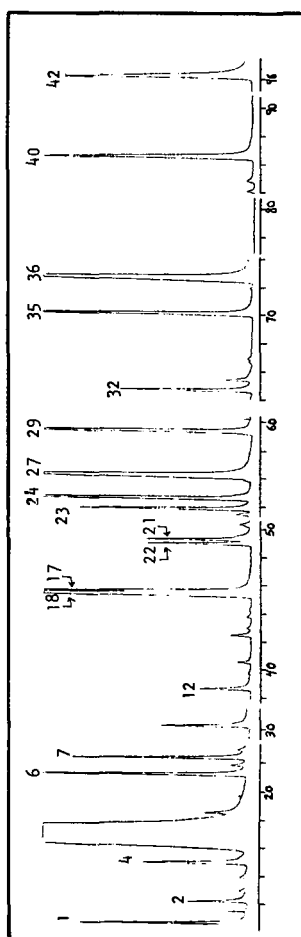


Figure 4. NEUTRAL FRACTION OBTAINED AFTER FRACTIONATION. CONDITIONS SAME AS IN TABLE 1.

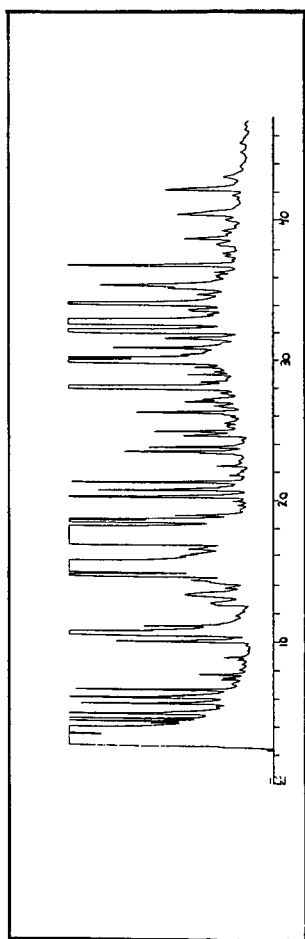


Figure 5. BASIC FRACTION ISOLATED FROM BRAZILIAN SRC (Mina do Leão).  
CONDITIONS SAME AS IN TABLE 1, EXCEPT TEMPERATURE PROGRAM 5°C/MIN.

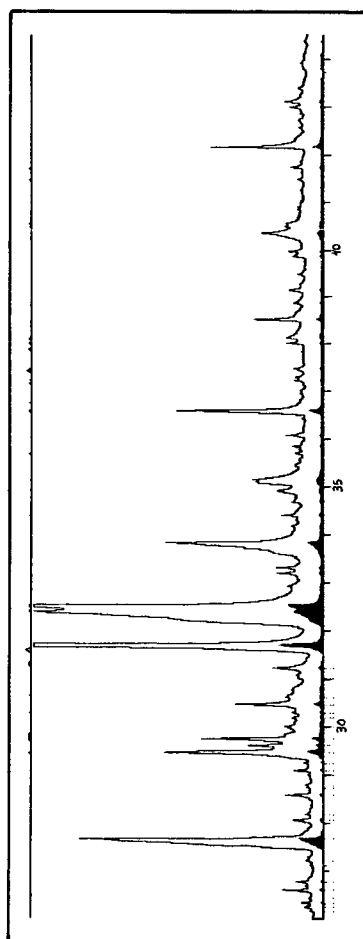


Figure 6. A PORTION OF THE TOTAL ION CHROMATOGRAM(T.I.C.) FOR BASIC FRACTION ISOLATED FROM  
Mina do Leão SRC. CONDITIONS SAME AS IN FIGURE 5.